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[Title of the Invention]

PROCESS FOR FABRICATING PHOTOELECTRIC CONVERSION DEVICE

[Scope of Claims]

[Claim 1] A process for fabricating a photoelectric  
5 conversion device, which comprises:

a step of forming a P-type non-single crystal  
semiconductor on a first electrode provided on a light-  
transmitting substrate;

10 a step of forming a 0.3 to 0.8  $\mu$  thick I-type non-single  
crystal semiconductor layer inside said semiconductor while  
adding a gaseous silicide together with a gaseous boride to a  
concentration of boron/silicon ratio of from 0 to 5 ppm; and

a step of forming an N-type semiconductor layer on said  
semiconductor layer;

15 wherein, in forming the I-type semiconductor layer,  
boron is added to the I-type semiconductor layer in the vicinity  
of the P-type semiconductor layer at a concentration of from  
0.05 to 5 ppm while continuously or substantially continuously  
decreasing the quantity of addition to produce a gradation in  
20 boron concentration within the I-type semiconductor layer.

[Claim 2] A process for fabricating a photoelectric  
conversion device as claimed in Claim 1, wherein a gaseous  
silicide  $\text{Si}_n\text{H}_{2n+2}$  (wherein  $n \geq 1$ ) or  $\text{SiF}_m$  (wherein  $m \geq 2$ ) and  
diborane are formed in the temperature range of from 100 to 400°  
25 C by plasma chemical vapor deposition or low pressure chemical  
vapor deposition.

[Detailed Description of the Invention]

The present invention relates to a photoelectric  
conversion device (photovoltaic conversion device; referred to  
simply hereinafter as a "PVC") having a PIN junction using a  
30 non-single crystal semiconductor into which hydrogen or a

halogen element is added, and particularly, a non-single crystal semiconductor containing silicon as the principal element.

An object of the present invention is to provide a PVC improved in conversion efficiency and to reduce the degradation thereof when light is irradiated thereto. Accordingly, an object of the present invention is to form a concentration gradation in the I-type semiconductor layer (hereinafter referred to simply as an "I layer") by continuously changing the addition of boron.

Thus, the present invention comprises a sept of fabricating a PVC having a PIN junction by employing particularly a plasma chemical vapor deposition (hereinafter referred to as a "PCVD") or low pressure chemical vapor deposition (hereinafter referred to as an "LPCVD"), thereby implementing a PIN junction by sequentially depositing a P layer, an I layer, and an N layer on a substrate. The process according to the present invention is characterized in that the I layer is formed at a predetermined thickness by using a boride such as diborane ( $B_2H_6$ ) simultaneously with a reactive gas for boron, such as silane ( $Si_nH_{2n+2}$ ) at a concentration of from 0 to 5 ppm, while controlling the quantity of addition on the P-type semiconductor layer side to fall in a range of from  $2 \times 10^{15}$  to  $2 \times 10^{17} \text{ cm}^{-3}$ , preferably in a range of from  $1 \times 10^{16}$  to  $4 \times 10^{16} \text{ cm}^{-3}$ , and reducing the quantity of addition on the N-type semiconductor layer side to a range of from 0 to  $1 \times 10^{15} \text{ cm}^{-3}$  by decreasing the flow rate of boron in such a manner that a gradually reducing concentration distribution is established.

Thus, as described in the foregoing, the present invention comprises a step of forming a P-type semiconductor layer comprising  $Si_xC_{1-x}$  (wherein,  $0 < x < 1$ ) on a first electrode using a clear conductive film (hereinafter referred to as a

"CTF") on a clear substrate and forming an I type semiconductor layer thereon by supplying silane containing diborane at a concentration of from 0.05 to 5 ppm (corresponding to an atomic concentration of from  $2 \times 10^{15}$  to  $2 \times 10^{17}$  cm<sup>-3</sup>), while establishing a graded concentration distribution which changes linearly or approximately linearly with a concentration difference of 1/5, preferably from 1/10 to 1/30, expressed in terms of ratio of a concentration in the NI junction side to that in the PI junction side.

By thus establishing a graded concentration distribution, the carriers excited by light, i.e., electrons or holes, are allowed to drift more easily. More specifically, the holes are attracted to the P-type semiconductor layer side, and the electrons are drifted to the N-type semiconductor layer side by providing an internal electric field. Thus, in this manner, a PVC whose output current is increased by 10 to 20% can be implemented as a result.

The depletion layer on the side to which light is irradiated becomes narrower due to deterioration induced by the photo irradiation effect (referred to hereinafter as "PIE"; also known as Staebler-Wronski effect). It is generally known that the conversion efficiency is lowered by 10 to 30% due to PIE. In the structure according to the present invention, however, no such degradation is observed. On the contrary, the efficiency of the present structure was found to increase by 5% in the initial stage. Although it decreased later by 0 to 5%, highly reliable characteristics with the fluctuation falling within a range of  $\pm 10\%$  is obtained even after continuously irradiating light for 1,000 hours.

A cross section view of a conventional PVC is shown schematically in Fig. 1(A). Referring to Fig. 1(A), a

conventional PVC comprises a clear substrate (1), a glass substrate in this case, having thereon a CTF (2) containing tin oxide as the principal component to provide a first electrode, and further thereon a P-type non-single crystal semiconductor such as  $\text{Si}_x\text{C}_{1-x}$  ( $0 < x < 1$ ) about 100 Å in thickness. About 0.5 μ thick I-type semiconductor layer (4) based on silicon and an N-type semiconductor (6) based on finely crystallized silicon are formed further thereon in this order on the P-type semiconductor layer. A back electrode is also provided to the structure. Considering the concentration distribution for the impurity in the I layer (4), which is the characteristic point of the present invention, however, a profile illustrated in Fig. 1(B) is obtained. Fig. 1(B) shows the concentration of boron (13) in the P-type semiconductor, the flat (constant) distribution of boron (17) in the I-type semiconductor, and that of phosphorus (15) in the N-type semiconductor.

In case where the P-, I-, and N-layers are formed separately in independent reactors, the distribution curve (13) shifts to that marked with (13'), and in case where the layers are formed in a same single reaction vessel, a distribution shown by curve (13'') is obtained.

The curves (13) and (17'') are continuous, however, the function of the I-layer is quite different from each other. The hatched region marked with (13''') indicates impurities present at a high concentration, and a layer prevents a depletion layer from being formed. Thus, a favorable concentration distribution curve is such expressed by (13'), which has no region (13''').

It can be seen therefore that the concentration of the impurity changes abruptly at the boundary of the PI junction or in the vicinity thereof. Accordingly, it has been regarded important in the conventional technology to incorporate boron in

such a manner that curves (13), (13'), and (17) are achieved. However, in the present invention, it is concluded that the conventional approach is insufficient for the generation of a drift electric field inside the I layer.

5 Fig. 1(C) shows the energy band structure in case boron is distributed in accordance with the profiles (13), (13'), and (17) as illustrated in Fig. 1(B).

10 In further detail, the structure comprises a CTF (2), a P layer (3), an I layer (4), an N layer (5), and a back electrode (6) in accordance with the structure illustrated in Fig. 1(A). Furthermore, the I layer comprises a depletion layer (55) due to the PI junction and a depletion layer (57) attributed to the NI junction. However, the depletion layers are independent to each other, and a region (56) having no internal electric field and which exhibits a flat energy band is found to  
15 be present in the central portion. Thus, it was found to be important to connect the two depletion layers (55) and (57) with each other by eliminating the region (56) having no internal electric field. In this manner, the carriers that generate with  
20 the irradiation of light can be rapidly separated for the two electrodes.

The present invention has been accomplished with an object to implement such a structure.

25 The present invention is described in further detail below.

Fig. 2 shows the concentration distribution curve for the impurities in PVC and I layer according to the present invention.

30 Referring to Fig. 2, Fig. 2(A) shows the vertical cross section view of the photoelectric conversion device according to the present invention. More specifically, it is composed of a

layered structure comprising a CTF (2) constituting a first electrode on a clear substrate (1), e.g., a glass substrate, about 100 Å thick P layer (3), an I layer (4) from 3,000 to 8,000 Å in thickness (it is formed at a thickness of 5,000 Å in this case), a 100 to 300 Å thick N layer (5), a CTF (6) constituting the second electrode, and a reflecting back electrode (6'). The CTF constituting the first electrode is a double-layered film composed of a 1,000 to 2,000 Å thick tin oxide film containing a halogen element or an ITO (indium oxide into which tin oxide is added at a concentration of 10% by weight of more) from 1,000 to 2,000 Å in thickness, and a tin oxide film from 200 to 400 Å in thickness. Boron may be added to the CTF, particularly in the vicinity of the P layer. CTF is fabricated by any one selected from the group of methods consisting of EB (electron beam deposition), PCVD, and LPCVD.

The figure specifically refers to a PVC having a single PIN junction. Accordingly, a multichamber apparatus in which reactors each corresponding for the P-, I-, and N-layers are established independent to each other but being connected with each other, was used. The details are to be described hereinafter, but the P layer was a non-single crystal semiconductor  $\text{Si}_x\text{C}_{1-x}$  ( $0 < x < 1$ ;  $x = 0.8$ ) containing boron with a maximum concentration in a range of from  $1 \times 10^{19}$  to  $6 \times 10^{20} \text{ cm}^{-3}$ . The I layer comprises an impurity concentrated in the vicinity of the PI junction at a concentration in a range of from  $2 \times 10^{15}$  to  $2 \times 10^{17} \text{ cm}^{-3}$ , and in the vicinity of the NI junction at a concentration of  $1 \times 10^{15} \text{ cm}^{-3}$  or lower, or at a concentration corresponding to 1/5 times, preferably, in a range of from 1/20 to 1/40 times, the concentration in the PI junction side. The impurity concentration between the PI and the NI junctions is gradually lowered so as to establish a uniform and constant

electric field density for the internal electric field. Microcrystalline N layer (5) was formed using gaseous silane, hydrogen, and phosphine at a ratio of silane/H<sub>2</sub> = 1/30 and PH<sub>3</sub>/silane = 1%. In this manner, absorption loss of light in N layer was suppressed as much as possible. The P, I, and N layers were each formed in separate reactors, using silane (SiH<sub>4</sub> or Si<sub>n</sub>H<sub>2n+2</sub>, n ≥ 2) as the gaseous silicide. The layers were deposited by means of PCVD (by applying electric energy of from 10 to 30 W, 13.56 MHz, and from 200 to 300 C for glow discharge) using monosilane or disilane, or by using diborane. Otherwise, LPCVD can be effected at 400 ± 50°C.

The back electrode was provided by forming a 900 to 1,300 Å thick ITO, preferably, a 1,050 Å thick ITO, as a CTF constituting the second electrode, and if necessary, by depositing further thereon a metal containing aluminum (or silver) as the principal component by vacuum deposition.

In this manner, a P layer having a wide optical gap E<sub>g</sub> of 2 eV or more ( $\sigma \geq 10^{-5} (\Omega\text{cm})^{-1}$ ), and an I layer having an E<sub>g</sub> of from 1.7 to 1.8 eV were established to provide a heterojunction PI. A microcrystalline or polycrystalline N layer was provided ( $\sigma = 10^0$  to  $10^2 (\Omega\text{cm})^{-1}$ ).

The I layer (4) comprises silicon as the principal component containing hydrogen at a concentration of from 2 to 20% by atomic for neutralizing the recombination centers. By using SiF<sub>2</sub> or a mixed gas of SiH<sub>4</sub> and SiF<sub>2</sub> as the starting gaseous silicide, it is possible to further add from 0.1 to 5% by atomic of fluorine into the I layer.

Diborane was also used. In the present case, a 100% gaseous monosilane was supplied as a gaseous silicide at a rate



of 20 cc/min, while supplying 20 ppm of diborane diluted with hydrogen. Diborane was thus added into the I layer in the vicinity of the boundary of PI junction at a concentration of from 0.05 to 5 ppm, i.e., at a rate of 0.05 cc/min to 5 cc/min. Specifically, for example, diborane was introduced at a concentration of 1 cc/min. This signifies that diborane is added at a concentration of 1 ppm ( $B_2H_6/SiH_4 = 20 \times 10^{-6} \times 1 \text{ (cc/min)} / 20 \text{ cc}$ ). Then, the concentration of diborane was reduced linearly. The silicon thus formed when adding 1 ppm of diborane was sampled, and was subjected to analysis for boron using an IMA (ion microprobe analyzer manufactured by CAMECA Ltd.). The boron content was not uniform for the samples, and was in the range of from  $2 \times 10^{16}$  to  $5 \times 10^{16} \text{ cm}^{-3}$ , for instance, about  $3 \times 10^{16} \text{ cm}^{-3}$ .

Fig. 2(B) shows the boron distribution in I layer shown in Fig. 1(A).

Referring to Fig. 2(B), the curve marked with (14) shows the concentration of boron in the I layer, and the  $B_2H_6/SiH_4$  ratio corresponding thereto.

Furthermore, in Fig. 2(B), the curve (13) shows the boron content in P layer, and curve (15) shows the concentration of phosphorus in the N layer.

The energy band diagram shown in Fig. 2(C) greatly differs from a one obtained in a conventional process.

Referring to Fig. 2(C), the numerals correspond to a first CTF (2), a P layer (3), an I layer (4), an N layer (5), a second CTF (6) for the back electrode, and a reflection electrode (6). It can be seen from the figure that the depletion layer (55) due to the PN junction is connected with the depletion layer (57) attributed to the NI junction inside the I

layer (4), and that hence no longer a region yielding a flat energy band as shown in Fig. 1 is present in the diagram. Thus, it can be seen that a drift electric field is formed. Accordingly, the electrons (67) and holes (68) that generate upon irradiating a light drift monotonously according to the internal electric field (i.e., the gradient of the band) towards the N layer (5) and the P layer (3).

Thus, it can be seen that the present invention is different from the prior art technologies and characterized in that a drift electric field is effectively generated in the I layer. It not only aims to neutralize the I layer that is rendered N conductive.

Fig. 3 shows a characteristic curve for a PVC having one PIN junction according to the present invention.

Referring to Fig. 3, the curve marked with (58) is for a conventional structure illustrated in Fig. 1 given for reference. The characteristic curve for the structure according to the present invention is marked with (59). The characteristics of the PVC are given below.

	<u>Prior Art</u>	<u>Present Invention</u>
Open Circuit Voltage (Voc (V))	0.89	0.92
Short Circuit Voltage (Isc (V)) (mA/cm <sup>2</sup> )	16.0	19.5
Curve Factor (FF (%))	61	68
Conversion Efficiency	8.7	12.2

( $\eta$  (%))

The characteristic values above are obtained in the case where AM1 (100 mW/cm<sup>2</sup>) is irradiated to an area of 3.5 mm x 3 cm (1.05 cm<sup>2</sup>).

It can be seen from the above results that the PVC of the drift type according to the present invention is capable of yielding a conversion efficiency higher by a large difference of 3.5% as compared with that of a conventional one.

Fig. 4 shows the results on reliability tests performed concerning PIE. More specifically, a light was irradiated at AM1 to the PVC with reference to Fig. 3. In a conventional PVC, the efficiency is observed to drop considerably for 15% after irradiating light for 10 hours. After 100 hours of continuous irradiation, about 20% of the initial efficiency is lost. Referring to Fig. 1(C), it can be seen that the boundary intensity changes abruptly. Accordingly, the depletion layer (55) at the PI junction is narrowed by PIE, and the flat region (56) is extended due to this abrupt change in boundary intensity.

In contrast to the case for a conventional PVC, the curve (61) in Fig. 5 obtained for the PVC according to the present invention shows that the efficiency slightly increases in the initial stage (about 10 hours). Although the efficiency decreases gradually in the later stage, the drop even after 1,000 hours of continued irradiation is within  $\pm 10\%$  of the initial conversion efficiency. A PVC using a non-single crystal semiconductor such as silicon was believed unsuitable for solar cells. However, the results obtained in the present invention

provides a fundamental solution for this problem. This is an unexpected characteristic of the present invention.

The profile shown in Fig. 5 is a modification of that shown in Fig. 2(B). More specifically, the I layer shown in Fig. 5(A) is fabricated by PCVD or LPCVD while gradually reducing the amount of boron by controlling the ratio  $B_2H_6/SiH_4$  in a manner similar to that with reference to Fig. 2. The resulting PVC yields an efficiency slightly lower, i.e., lower by about 0.5%, than that obtained in accordance with Fig. 2, however, the other characteristics are approximately the same.

Fig. 5(B) shows a case obtained by adding boron from the PI junction up to a point at a distance of 4,000 Å from the junction, and then stopping the addition in the remaining region of about 1,000 Å. In this manner, the boron content in the N layer is suppressed to  $10^{14} \text{ cm}^{-3}$  or lower to further increase the open circuit voltage in the vicinity of the N layer. Thus, the open circuit voltage was further increased by 0.01 V. The values for conversion efficiency fluctuated in the same manner as illustrated in Fig. 2(B), and the distribution was the same as that shown in Fig. 2(B).

It can be seen from the graph in Fig. 6 showing a substantially linear distribution that it is different from that illustrated in Fig. 1(B). When the boron concentration is increased to  $2 \times 10^{17} \text{ cm}^{-3}$  or higher, a sufficiently low depletion layer cannot be obtained at the vicinity of the PI junction. This results in a reversely impaired efficiency with a drop of 0.5 to 2.0%. In case the boron concentration is lowered to  $1 \times 10^{15} \text{ cm}^{-3}$ , on the contrary, a sufficient drift was not obtained.

In the present example, unavoidable phosphorus and oxygen are present in the I layer to yield a background level in the range of from  $1 \times 10^{14}$  to  $10 \times 10^{14} \text{ cm}^{-3}$  and from  $1 \times 10^{18}$  to

$10 \times 10^{18} \text{ cm}^{-3}$ , respectively. By reducing the concentration of unavoidable phosphorus and oxygen to a level of 1/10 to 1/100 of the present level, the addition of boron can be further lowered to about 1/5 of the present required concentration of  $2 \times 10^{15} \text{ cm}^{-3}$ .

In the foregoing explanation, a PVC comprising a single PIN junction is described. However, the present invention can be applied to a case in which two or more of such PIN junctions are superposed in such a manner to obtain a PINPIN.... PIN junction. The present invention can be then applied to at least one I layer of the structure.

[Brief Description of the Drawings]

Fig. 1 shows a vertical cross section view of a conventional photoelectric conversion device. The impurity concentration distribution and energy band diagram are also given.

Fig. 2 shows a vertical cross section view of a photoelectric conversion device according to the present invention. The impurity concentration distribution and energy band diagram are also given.

Figs. 3 and 4 each show the photoelectric conversion characteristics of the photoelectric conversion device according to the present invention and to a prior art technology.

Fig. 5 shows an impurity concentration distribution for another photoelectric conversion device according to the present invention.

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